

Bipolar single-wall carbon nanotube field-effect transistor

Bakir. Babić, Mahdi. Iqbal, and Christian. Schönenberger*

Institut für Physik, Universität Basel,

Klingelbergstr. 82, CH-4056 Basel, Switzerland

(Dated: February 1, 2008)

Abstract

We use a simultaneous flow of ethylene and hydrogen gases to grow single wall carbon nanotubes by chemical vapor deposition. Strong coupling to the gate is inferred from transport measurements for both metallic and semiconducting tubes. At low-temperatures, our samples act as single-electron transistors where the transport mechanism is mainly governed by Coulomb blockade. The measurements reveal very rich quantized energy level spectra spanning from valence to conduction band. The Coulomb diamonds have similar addition energies on both sides of the semiconducting gap. Signatures of subbands population has been observed.

PACS numbers: 73.61.Wp,72.80.Rj,73.63.Fg,73.40.Qv,73.63.Nm,73.23.Hk

*Electronic address: Christian.Schoenenberger@unibas.ch; URL: www.unibas.ch/phys-meso

Single wall carbon nanotubes (SWNTs) are chemically derived self-assembled solid molecules with fascinating electronic properties [1]. Their rich variety of band structure (metallic, semiconductor) might revolutionize nano-electronics. Recently, not only an extensive spectrum of quantum phenomena have been demonstrated with SWNTs [2, 3, 4, 5], but they have also been used as functional electronic devices in the form of field effect transistors (FETs) [6, 7]. The as-grown SWNT FETs were found to be unipolar p-type, i.e. no electrical current flows even at large positive gate voltages. The p-type nature of nanotubes (NTs) has been attributed to charge transfer caused by either oxidizing molecules adsorbed to the NTs [8], or the difference in workfunctions between NTs and metallic contacts (mostly Au) [6]. The unipolarity, on the other hand, has been attributed to the presence of Schottky barriers at the metal-nanotube contacts [9]. Though as-grown SWNTs are p-type, n-type unipolar conductance has been demonstrated by either chemical doping [10] or an annealing treatment in an inert environment [11]. It remains, however, challenging to realize bipolar SWNT FETs which operate without any additional treatment and use conventional back-gating. Bipolar SWNT FETs has been demonstrated on large-diameter SWNTs [12], and recently also on small-diameter SWNTs by using strong-coupling gates [13]. Here we report on electronic transport measurements on as grown SWNTs which show bipolar FETs action.

SWNTs are synthesized by chemical vapor deposition (CVD) following the method of Hafner et al. [14]. In all our studies we used SWNTs having diameters of 2 nm or less, as inferred from AFM height measurements. Our devices are prepared on highly doped ($< 0.02 \Omega\text{cm}$) and thermally oxidized (400 nm) Si wafers. The substrate is used as back gate in electrical measurements of the final devices which are obtained as follows: The substrate is covered with a layer of polymethylmethacrylate (PMMA) in which windows are patterned by electron beam lithography. Then, a catalyst suspension consisting of 1 mg iron nitrate seeds ($\text{Fe}(\text{NO}_3)_3$) dissolved in 10 ml of isopropanol is poured into the predefined trenches. The PMMA is then removed in acetone, leaving isolated catalyst islands ($5 \times 10 \mu\text{m}^2$) on the surface. The CVD growth is performed in a quartz-tube furnace at 800 °C and atmospheric pressure using a gas mixture of ethylene, hydrogen and argon with respective flow rates of 2, 400, and 600 cm³/min. During heating and cooling of the furnace, the quartz tube is continually flashed with argon to avoid contamination of the tubes. The as-grown SWNTs are then contacted in a conventional lift-off process with two metal electrodes per SWNT, spaced 1 μm apart. As electrode material Ti/Au bilayer is used, leading to contact resistances

of $\approx 40 \text{ k}\Omega$ at room temperature. Figure 1a illustrates schematically a SWNT device. An atomic force microscopy (AFM) picture is displayed in figure 1b. The diameter of the nanotubes is determined from the measured height using AFM in tapping mode.

Once the samples are made, semiconducting and metallic tubes are distinguished by the dependence of their electrical conductance G on the gate voltage V_g , measured in a wide temperature range of $0.3 \dots 300 \text{ K}$. Figure 2 shows $G(V_g)$ for a semiconducting SWNT at moderate temperatures of $T = 40$ and 60 K . Starting from $V_g = -10 \text{ V}$, G decreases with increasing V_g indicating p-type behavior, while above $V_g \approx 4 \text{ V}$ G increases indicating n-type behavior. In between these two regions the conductance is low, which suggests carrier depletion. This low conductance region corresponds therefore to the gap. The charge-neutrality point for this sample lies at $V_g = 2.5 \text{ V}$. Taking the respective capacitances into account (see below), this corresponds to a Fermi energy of $E_F = 0.5 \text{ eV}$. In general, charge-neutrality points vary between $E_F = -0.5 \text{ eV}$ and 0.5 eV .

Our finding demonstrates that the SWNT devices are bipolar transistors. Taking a linear approximation for $G(V_g)$ (dashed lines in figure 2), we obtain a relatively high average carrier mobility of $\mu \approx 800 \text{ cm}^2/\text{Vs}$.

$G(V_g)$ is not strictly linear, but shows several pronounced humps (see arrows in figure 2) which we attribute to van Hove singularities (VHS) in the 1-dimensional (1D) density-of-states (DOS). Conductance peaks are expected, if the contacts couple weakly to the NTs (tunnelling contacts) and if the band structure of the NT can rigidly move while sweeping V_g . The measured low conductance $\approx 10^{-3} \times 2e^2/h$ of this device is in favor of tunnelling contacts. The observed humps in $G(V_g)$ are separated by $\Delta V_g \approx 2 \text{ V}$. This relates to an energy interval of $\approx 0.4 \text{ eV}$. The VHS are smeared and do not appear symmetrically with respect to the semiconducting gap. We attribute this to defects which modify the band structure, resulting in a broadening of the VHS.

We now turn to low-temperature measurements $T \leq 4 \text{ K}$. Figure 3 shows $G(V_g)$ and a greyscale representation (inset) of the differential conductance dI/dV as a function of V_g and applied transport voltage V_{sd} of a SWNT device at $T = 2 \text{ K}$. The large white zone in the middle of the greyscale plot corresponds to a non conducting region related to the semiconducting gap (SG). The drawn thick lines at the edges are guides to the eye. Their vertical extensions intersect around $V_{sd} \cong 0.6 \text{ eV}$, which is a direct estimate of the gap energy. On both sides of the SG Coulomb blockade diamonds (CBD) of varying size are

observed (we refer to the term ‘diamond’, although the blockade region is not composed of a series of neat diamonds). Though the addition energy E_{add} is seen to fluctuate in between 2.5 and ≤ 20 meV, there is a general trend, indicated by the thin curved lines. Close to the gap E_{add} is large and decays to smaller value for lower (higher) V_g on the p (n) side. As a reference we expect $E_{add} \sim 4$ meV for an undisturbed 1 μm long SWNT. Because E_{add} is determined by the sum of the single-electron charging energy U_c and the 0D level spacing ΔE , U_c and ΔE must depend on V_g , at least in the vicinity of the SG. This is not expected for an ideal (defect-free) semiconducting NT for the following reason: At the onset of the conduction or valence band, the 1D DOS is expected to be very large (VHS), since the band dispersion is parabolic to first approximation. If the nanotube can be considered a single quantum dot extending from one contact to the other, the 0D level spacing should be very small, i.e. $\Delta E = 0$ to first approximation. Provided the added charge can spread homogeneously along the whole tube, a constant charging energy U_c is expected. Hence, we would expect a constant addition energy in case of an ideal defect-free tube. The observed discrepancy can be resolved if (weak) disorder is taken into account. Disorder will distribute the states over some energy interval leading to the observed broadening of the VHS. Moreover, this results in a smooth onset of the DOS and consequently in a relatively large 0D level-spacing. Disorder also (partially) localizes the wavefunctions, leading to both increased ΔE and U_c .

Next we focus on the region far away from the SG where ideally the 0D wavefunctions are extended, i.e. one quantum dot (QD), and where the constant interaction model should yield a good approximation to single-electron charging effects. The charging energy is then given by the capacitances determined by the geometry of the device. Figure 4 presents three greyscale plots of the differential conductance dI/dV , 4a and b for one semiconducting NT and 4c for another metallic NT with identical contact spacing. The latter is shown as reference. Figure 4a and b correspond to conduction in the p and n region, respectively. Both have been measured around $|V_g| \approx 10$ V corresponding to ≈ 1000 added carriers.[15] If we compare with our metallic reference, the Coulomb blockade (CB) diamonds are less regular in the semiconducting case. Importantly, however, they are similar in all respects on the n and p side. The irregularity of the CB and the fact that the gap most often does not close implies that the NT does not act as a single QD. The low maximum conductance of $\leq 0.025 e^2/h$ observed in the linear conductance in figure 3 supports this finding. Based on the maximum E_{add} , three QD’s is an upper limit. Hence, even at large gate voltage,

defects are still effective in dividing the tube into smaller segments. The CB-pattern on the n-side seems to show a beating pattern repeating after $\approx 6 - 7$ added charges. A strong beating pattern on the n-side has been observed before [9] and has been attributed to the formation of a small quantum dot in the vicinity of one of the contacts. Since the metal contact has a larger workfunction than the NT, p-doping is expected at the contacts. If this charge transfer is large enough a p-type metal-insulator-semiconductor contact arises. As the p-type puddle is well buried below the contacts it possibly cannot be depleted by the gate whose field is screened by the contacts. Then, the p-type puddle remains even if the bulk NT is n-type.

The analysis of CB diamonds permits to extract the factor α [16] which measures the effectiveness of the coupling capacitance between the tube and the gate, i.e., $\alpha = C_g/C_\Sigma = U_c/\Delta V_g$. Here, C_g is the gate capacitance, C_Σ the total capacitance (gate plus contacts), $U_c = e^2/C_\Sigma$ the charging energy, and ΔV_g the single-electron period in gate voltage. We estimate the charging energy from the averaged value of the addition energy of a set of Coulomb diamonds. This results in $U_c \approx 2.5$ meV within a gate-voltage period of $\Delta V_g = 12$ meV, from which we deduce $\alpha \approx 0.2$. Note, that this is a very high coupling effectiveness for a nanotube whose gate-electrode is as much as 400 nm away! We take this coupling effectiveness to estimate the size of the semiconducting gap E_g using the measurement of figure 2 or figure 3. The SG corresponds to a gate-voltage window of $\Delta V_{g-gap} \approx 4 - 5$ V leading to $E_{gap} = e\alpha\Delta V_{g-gap} = 0.8 - 1.0$ eV. This value is comparable to the one given above and is in fair agreement with the reported 0.8 eV for a 1 nm diameter SWNT [17]. From α and U_c we obtain for the capacitances $C_g \approx 12.8$ aF and $C_\Sigma \approx 60$ aF. C_g is in reasonable agreement with the estimated geometrical capacitance $C_{geometry} = 2\pi L\epsilon_r\epsilon_0/\ln[2L/d]$ (L and d are the length and the radius of the nanotube, respectively), yielding 29 aF. The factor of 2 difference may originate from the partial screening by the contacts.

The value of α found here is one of the largest values reported so far [11]. As a reference to our study on semiconducting SWNTs, we have investigated metallic tubes of similar length too. Contrary to semiconducting NTs we observe regular Coulomb blockade diamonds in metallic SWNTs (see figure 4c). At the edges of each diamond, parallel and sharp lines are visible reflecting excited states of the nanotube quantum dots. The charging energy and the single electron level spacing are found to be 3 meV and 1 meV, respectively. The latter is in good agreement with the contact separation of $L \approx 1 \mu\text{m}$. This strongly suggests, that

metallic SWNTs behave like single quantum dots, unlike semiconducting SWNTs. In addition, the coupling to the gate shows the same large value of $\alpha \sim 0.2 - 0.3$ and corroborate the universal aspect of the high gate effectiveness independent of the nature of the tubes. We think that the use of hydrogen during the CVD growth is of crucial importance. It passivates SiO_2 dangling bonds and helps to reduce the number of charge traps in the substrate. Consequently, it leads to a better coupling of SWNT to the back-gate and therefore to bipolar action of the devices.

In conclusion, these experiments demonstrate that CVD-grown SWNTs can display a very high coupling efficiencies to a back gate without using any additional post-treatment. Due to the large coupling efficiency semiconducting SWNTs can be continuously gated from p to n-side and therefore act as bipolar FETs. At low-temperature, semiconducting SWNTs are strongly affected by disorder, which (partially) splits the tube in a couple of quantum dots. As the maximum number of dots is smaller than 3 for our SWNTs with $1\ \mu\text{m}$ contact separation, it appears that single quantum dots should be feasible for smaller contact separation.

Acknowledgments

We acknowledge M.R. Buitelaar for fruitful discussions and T. Nussbaumer for technical assistance. This work is supported by COST (BBW), the NCCR on Nanoscience and the Swiss NFS.

- [1] See e.g., Dresselhaus M S, Dresselhaus G, Eklund P C 1996: *Science of Fullerenes and Carbon Nanotubes* (New York, Academic Press, 1996)
- [2] Dekker C 1999 *Physics Today* **52** (5) 22
- [3] Kong J *et al* 2000 *Phys. Rev. Lett.* **87** 106801
- [4] Bockrath M *et al* 1999, *Nature* **397** 598
- [5] Liang W *et al* 2001 *Nature* **411** 665
- [6] Tans S J *et al* 1998 *Nature* **393** 49
- [7] Martel R, Schmidt T, Hertel T, and Avouris P 1998 *Appl. Phys. Lett.* **73** 2447
- [8] Zhou C *et al* 2000 *Science* **290** 1552

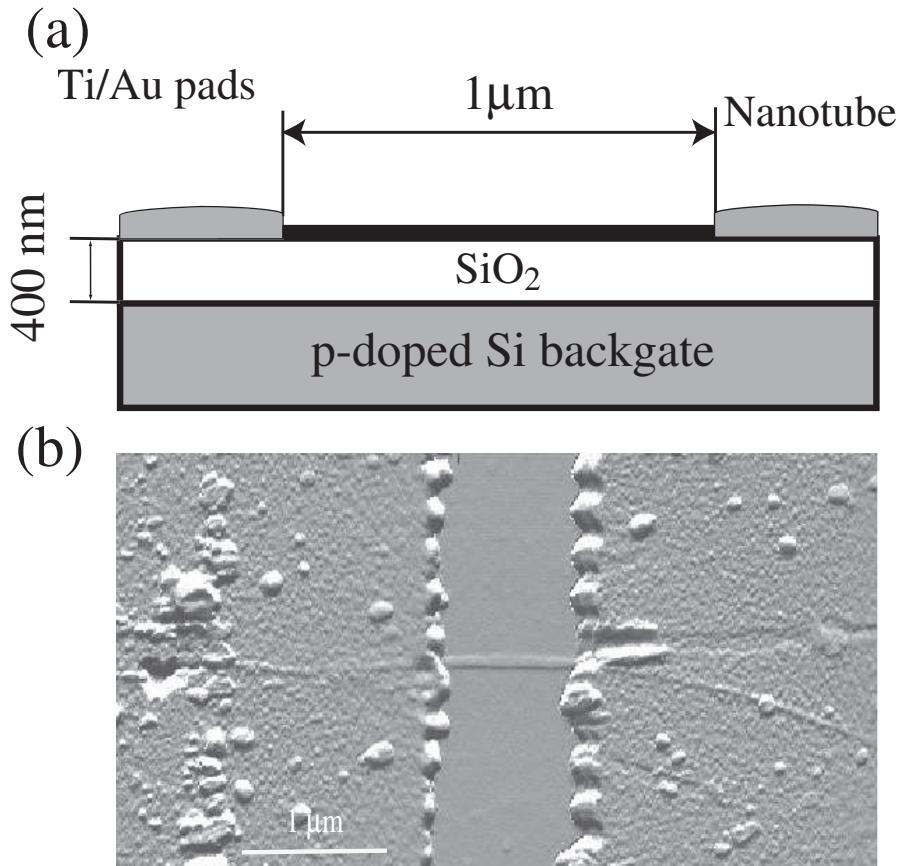


FIG. 1: (a) Scheme of a SWNT device contacted by two Ti/Au electrodes. The Si substrate is used as back-gate. (b) Atomic force microscopy (AFM) image of a SWNT bridging between the two electrodes.

- [9] Park J and McEuen P 2001 *Appl. Phys. Lett.* **79** 1363
- [10] Bockrath M *et al* 2000 *Phys. Rev. B* **61** R10606
- [11] Radosavljević M, Feitag M, Thadani K V and Johnson A T 2002 *Nano Lett.* **2** No. 7 p 761
- [12] Javey A, Shim M and Dai H 2002 *Appl. Phys. Lett.* **80** 1064
- [13] A Bachtold, P Hadley, T Nakanishi and C Dekker 2001 *Science* **294** 1317
- [14] Hafner J H, Bronikowski M J, Azamian B R, Nikolaey P, Rinzler A G, Rinzler D T, Smith K A and Smalley R E 1998 *Chem. Phys. Lett.* **296** 195
- [15] From gate period for CB peaks we add approximately 100 electron per one Volt at the gate.
- [16] Beenakker C W J 1991 *Phys. Rev.* **44** 1646
- [17] Wildoer J *et al* 1998 *Nature* **391** 59

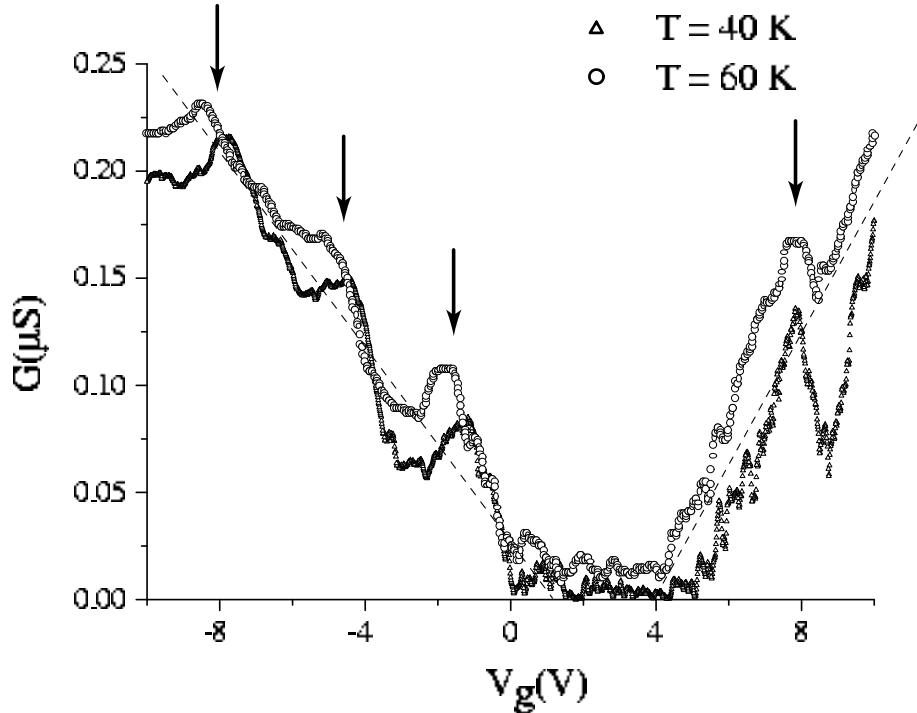


FIG. 2: Two-terminal conductance G as a function of gate-voltage V_g for a semiconducting SWNT at moderate temperatures of $T = 40$ and 60 K , respectively. The peaks in G (arrows) are attributed to van Hove singularities in the DOS.

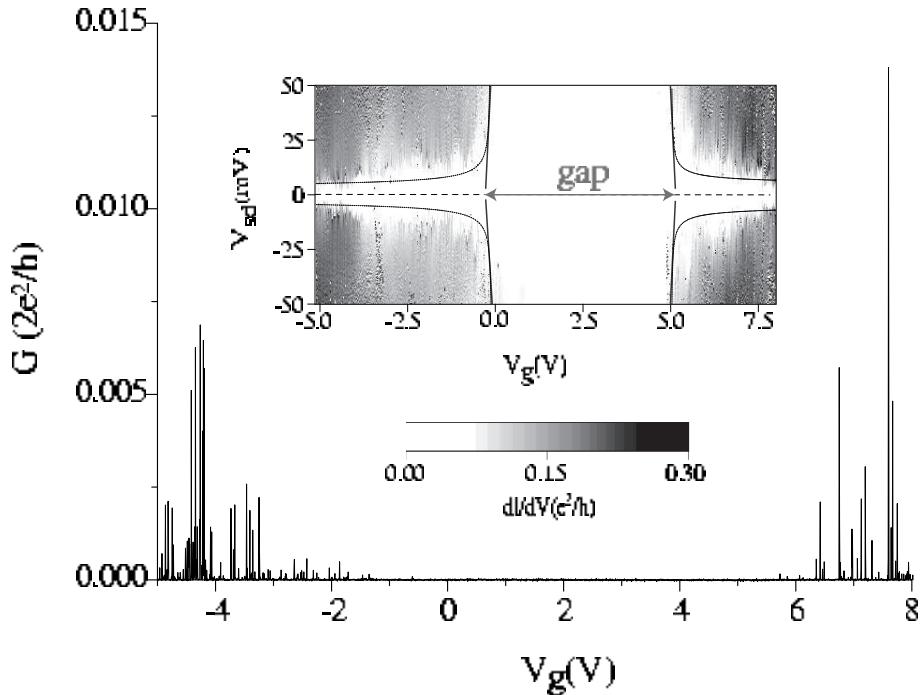


FIG. 3: Linear conductance G as a function of gate voltage V_g (main plot) and greyscale representation of the differential conductance dI/dV as a function of V_g and applied source-drain voltage V_{sd} (inset) at 2K for a SWNT device. White regions correspond to zero and dark regions to high conductances (maximum $0.3 e^2/h$). The semiconducting gap (SG) is clearly visible as a large non-conducting region in the inset. Coulomb oscillations peaks are observed on the p (left) and n (right) side of the semiconducting gap.

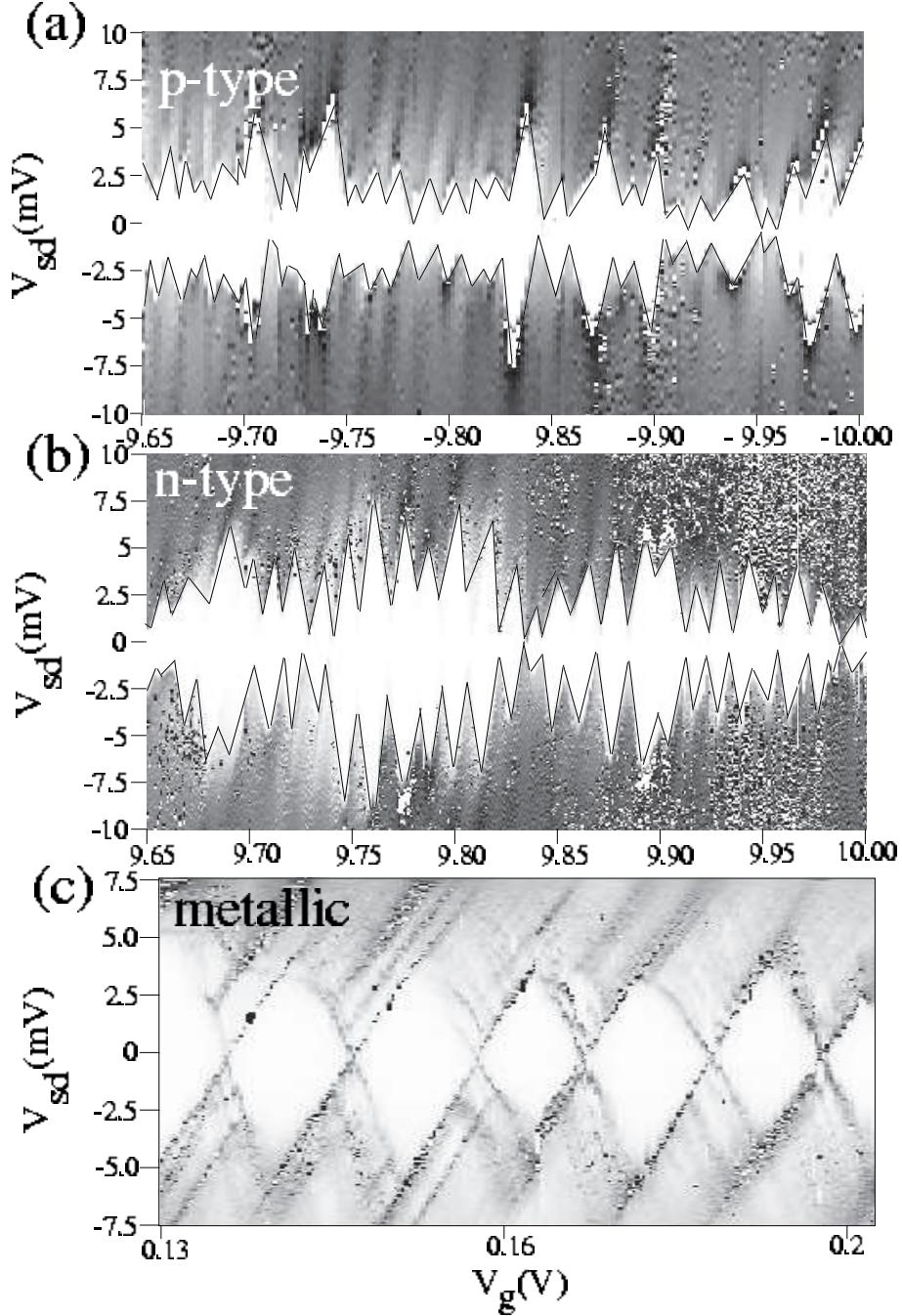


FIG. 4: Differential conductance (dI/dV) plots as a function of V_g and V_{sd} . White corresponds to $dI/dV = 0$, and black to the maximum conductance of $0.3 e^2/h$. (a) and (b) have been measured on one semiconducting SWNT in the p region (a) and n region (b) at 2 K. As a reference a similar plot of another metallic SWNT measured at 0.3 K is shown in (c). While excited states can clearly be seen in (c), they appear to be absent in (a) and (b). Furthermore, while (c) displays a regular Coulomb blockade (CB), it is irregular in (a) and (b). In all cases strong coupling to the gate is inferred.